

**Adsorption of Nonionic Oxyethylated Sulfonamides onto Sand and Kaolin  
from Aqueous Solution**

# Adsorption of Nonionic Oxyethylated Sulfonamides onto Sand and Kaolin from Aqueous Solution<sup>1</sup>

## ABSTRACT

Nonionic surfactants continue to be used as soil conditioners, principally as wetting agents, but optimum surfactant chemical structure has not as yet been completely established. This research using nonionic surfactants, alkyl substituted polyoxyethylated phenylsulfonamides, has determined the effect of varying the ethoxy content and the alkyl side chain on three surfactant characteristics, i.e., adsorption, wetting, and dispersion. It was found that surfactant adsorption on sand and kaolin, two soil components, at a constant pH of 6.0 decreased with higher surfactant ethoxy content. Changing the alkyl side chain from C<sub>6</sub> to C<sub>8</sub> to C<sub>10</sub> increased the apparent surfactant attraction for the adsorbent surface but not the total amount of surfactant adsorbed. The amount of surfactant adsorbed determines the final nature of the adsorbent's surface and its hydrophobic or hydrophilic character. Thus, the wetting and dispersing properties of soil components can be set by the amount of surfactant adsorbed.

**Additional Index Words:** soil conditioner, wetting agent, surfactant structure.

Hampson, J.W., D.G. Cornell, and T.J. Micich. 1986. Adsorption of nonionic oxyethylated sulfonamides onto sand and kaolin from aqueous solution. *Soil Sci. Soc. Am. J.* 50:1150-1154.

NONIONIC SURFACTANTS are widely used in agriculture as emulsifiers for herbicide and insecticide sprays, and as soil conditioners to enhance soil wetting. The mechanism by which nonionic surfactants adsorb from aqueous solution onto soils and how structure affects this mechanism has not been fully elucidated. The effect of surfactant ethylene oxide (ethoxy) content and hydrocarbon chain length on soil wetting has been studied (Micich and Linfield, 1984; Weil et al., 1979). An optimum ethoxy content and hydrocarbon chain length was found for each series of nonionic surfactants that gave select soil wetting and rewetting properties. The adsorption of nonionic surfactants onto soils has also been investigated (Law and Kunze, 1966; Valoras et al., 1969) and a great deal of important information about the performance of nonionic surfactants as soil wetting agents has also been provided (Letey, 1975; Letey et al., 1975).

Nonionic surfactants (oxyethylated type) adsorb onto adsorbents in either of two ways, i.e., by hydrophilic bonding of the surfactant's ethoxy groups or by hydrophobic bonding of the surfactant's hydrocarbon chain (Rosen, 1978). In the previous work on oxyethylated sulfonamides (Micich and Linfield, 1984), the importance of nonionic surfactant adsorption onto soil was discussed, but the mechanisms by which these

reactions occur were not presented. In preliminary studies of the interaction of a few of these surfactants with naturally occurring soils, we found complex behavior and exceedingly high levels of sorption. It was clear that a systematic study of the interaction of oxyethylated sulfonamides with the various components of soil would be required in order to understand the action of these surfactants in field applications. In this manuscript we report our results with sand and non-swelling clay, whose surface properties presumably are less complex than for swelling clays and the organic fraction of soils. We will discuss possible mechanisms and suggest the type of surfactant structure that best imparts good wettability, and strong adsorption onto these simple systems. Extensions of these studies to more complex systems is under way. Clearly, an understanding of chemical structural effects on surfactant adsorption from solution is important in soils as well as in other fields, i.e., detergency (Schott, 1968), flocculation (Kuno and Abe, 1961; Abe and Kuno, 1962), and oil recovery (Hsiao and Dunning, 1955; Figdore, 1982).

## MATERIALS AND METHODS

ASTM standard sand C190, 0.85- to 0.60-mm sieve opening, Ottawa standard, was obtained from A.H. Thomas Co., Swedesboro, NJ.<sup>2</sup> The sand particles are composed almost entirely of naturally rounded grains of nearly pure quartz graded to pass through a 850- $\mu$ m (no. 20) and be retained on a 600- $\mu$ m (no. 30) sieve. The surface area (Krypton BET) was 52 m<sup>2</sup>/kg. Kaolin, labeled Hydrite R, was obtained from Georgia Kaolin, Elizabeth, NJ. Median particle diameter was given as 0.77  $\mu$ m and surface area was 10 000 m<sup>2</sup>/kg (BET nitrogen). Hydrites are water processed to reduce soluble salts to extremely low levels. Kaolin particles are thin, flat, hexagonal plates with a moisture content of no more than 0.01 kg/kg. The nonionic surfactants were tertiarybutylphenyl C<sub>6</sub>, C<sub>8</sub>, and C<sub>10</sub> polyoxyethylated sulfonamides where the number of ethoxy groups varied from 5 to 19 and were prepared as previously described (Micich and Linfield, 1984). Distilled water was used throughout for all solutions.

Isotherms were obtained by determining surfactant concentration in the aqueous phase of a sand/clay suspension before and after adsorption at room temperature (22  $\pm$  2°C). The difference was taken as a measure of the amount of surfactant adsorbed by the sand or clay. A 1 to 2 mM surfactant solution was prepared as the stock solution and all other surfactant solution concentrations were made by dilution. Mixtures of adsorbent-surfactant solutions were shaken periodically for 24 h to establish equilibrium. Portions of the mixture of kaolin and surfactant solutions required centrifugation in order to obtain a clear sample solution for spectrometry. Spectra were obtained with a Perkin-

<sup>1</sup> Contribution of USDA-ARS, Eastern Regional Research Center, Philadelphia, PA 19118. Received 13 Jan. 1986.

<sup>2</sup> Research Chemists.

Reference to brand or firm name does not constitute endorsement by the USDA over others of a similar nature not mentioned.

Elmer U.V.-Vis Model 559 spectrophotometer using 1-cm cells and a scanning range from 300 to 200 nm. Absorbance peaks for the surfactants were between 225 and 235 nm. A blank spectrum from water-sand or water-clay mixtures without surfactant was subtracted from the sample spectra. Surfactant adsorbed was calculated as milligram adsorbed per gram adsorbent, converted to milligrams adsorbed per square meter and plotted vs. equilibrium concentration of surfactant. Adsorption isotherms are shown in Fig. 1, 2, and 3. For those isotherms that appeared to be of the Langmuir type (Fig. 2 and 3), the area per surfactant molecule adsorbed was calculated from the linear form of the Langmuir equation. For experiments with sand each sample contained 50-g sand in 50-mL surfactant solution, and for kaolin, 0.5-g kaolin in 50-mL surfactant solution. The pH of all solutions was 6.0.

Capillary rise was used to determine the effect of surfactant treatment on the sand's wettability. For this procedure, a vertical glass tube (diam 15 mm, length 12 cm) was inserted into untreated sand to a depth of 2 cm such that the levels of the sand inside and outside of the tube were the same. The remainder of the tube was then filled with air-dried surfactant treated sand. Water was added to the untreated sand and the rise in the water level inside the glass tube with the treated sand over a 5-min period was determined. The vertical water rise on a blank of untreated sand mixed with distilled water and air-dried was used as the reference.

Dispersion of surfactant treated kaolin was evaluated by measuring sedimentation volume and turbidity. Both determinations were made using a series of glass stoppered graduate cylinders each with 0.5-g kaolin and 50 mL of a surfactant solution that varied in concentration from 20 to 320 mg/L. The samples were agitated by inverting the cylinders several times and were then allowed to stand undisturbed during the remainder of the test. All samples were compared to a blank of 0.5-g kaolin suspension in 50 mL of distilled water with the results recorded as a function of time. Sedimentation volume difference was measured in cubic centimeters as the difference between sediment bed volumes of kaolin suspension with and without surfactant. Turbidity was measured on an arbitrary scale of +5 to -5 as more or less turbid than the kaolin blank, which was assigned a value of zero. Both the sediment and turbidity data were obtained on suspensions that were allowed to settle for 15 min.

## RESULTS AND DISCUSSION

The adsorption of four polyethoxylated butylphenylsulfonamides ( $C_6$  alkyl side chain) onto sand and kaolin as a function of increasing surfactant ethoxy (EO) content is illustrated in Fig. 1. The isotherms show that as the number of EO groups ( $n$ ) in the molecule is increased, there is a corresponding decrease in surfactant adsorption on both sand and kaolin. The surfactants appear to exhibit neither Freundlich nor Langmuir type adsorption, but give isotherms more closely resembling the S type in Giles classification. This type is characterized by an initial portion convex to the concentration axis suggesting weak surface attraction, with a steep rise in adsorption at higher concentrations due to the lateral association of surfactant hydrocarbon chains on the adsorbent surface (Parfitt and Rochester, 1983). Surfactants with strong surface attraction exhibit isotherms in which the adsorption rises steeply from the origin with increasing concentration of the surface active species, giving rise to a curve that is concave to the concentration axis (Parfitt

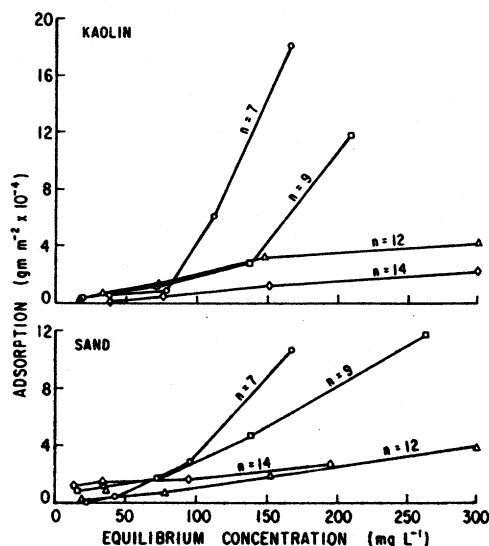


Fig. 1. Adsorption isotherms of (N-hexyl)(N-polyethoxylated)p-t-butylphenylsulfonamides on sand and kaolin at pH 6.0 in aqueous solution; ( $n$ ) equals number of ethoxy groups.

and Rochester, 1983) According to this scheme, the isotherms in Fig. 1 indicate that the surfactants have a relatively low affinity for the surface with very little adsorption below 40 mg/L. Significant adsorption occurs only above 100 mg/L, where the steep rise in the isotherms suggest that the coverage is greater than for a monolayer of molecules lying flat.

Sulfonamide surfactant adsorption probably takes place through electrostatic forces because of the polar nature of sand's and kaolin's surfaces. At pH 6.0, both sand (silica) and kaolin (hydrated aluminum silicate) are primarily negatively charged as both are well above their zero point of charge (ZPC), i.e., pH 2.0 for silica, and 3.5 for kaolin. Therefore, the surfactant EO groups, which can be protonated and thus positively charged, may be adsorbed onto the surface through electrostatic attraction. At low concentrations, the entire molecule may lie flat on the surface. At higher concentrations the hydrocarbon portion may be forced into the aqueous media, promoting lateral association of the surfactant molecules through hydrophobic interaction. This would promote increased adsorption at high concentration, consistent with the data shown in Fig. 1. Thus at high surfactant concentration the adsorbent's surface should be hydrophobic, making capillary absorption of water by sand more difficult and kaolin dispersion less likely due to reduction of negative charge by adsorbed  $EOH^+$  groups and hydrophobic interaction of the protruding hydrocarbon chains. Arrangements of the adsorbed species illustrating these points have been described (Clunie and Ingram, 1983).

Table 1 shows that the hexyl derivatives in general and the surfactant with seven ethoxy groups in particular imparts more water repellency to the sand's surface than other compounds listed. The capillary rise value of -1.0 for the  $n = 7$  derivative was the lowest found. Data from kaolin sedimentation volume differences and turbidity measurements also show less dispersion for  $n = 7$  than the blank. This suggests that the surfactant aids in the coalescence of kaolin parti-

Table 1. Properties and adsorption behavior of alkyl substituted polyethoxylated *p*-*t*-butylphenylsulfonamides on sand and kaolin.

R	n	Appearance†	HLB‡	MW§	nm²¶	nm²#		Cap. rise††	Kaolin sed. vol. dif.‡‡	Kaolin turb.§§
						Sand	Kaolin			
C <sub>6</sub>	7	Cloudy + ppt	10.2	606	0.98			-1.0	-1.5	-4
C <sub>6</sub>	9	Cloudy	11.5	694	1.08			-	-1.5	-5
C <sub>6</sub>	12	Almost clear	12.8	826	1.21			-	-0.5	-3
C <sub>6</sub>	14	Clear	13.5	914	1.30	8.30		+0.6	-1.0	-5
C <sub>8</sub>	5	Cloudy + ppt	8.1	546	0.92	-	-	-	0.0	0
C <sub>8</sub>	9	Hazy clear	11.0	722	1.11	1.40 (1.24)	1.14 (1.06)	+0.8	-3.0	+2
C <sub>8</sub>	15	Clear	13.4	986	1.36	2.16 (2.22)	3.56 (2.76)	+0.9	-1.0	+1
C <sub>8</sub>	19	Clear	14.4	1162	1.53	2.89 (2.49) (2.37)	4.83 (-)	+0.8	-1.0	-2
C <sub>10</sub>	5	Cloudy + ppt	7.7	574	0.95	-	-	-	-0.5	0
C <sub>10</sub>	9	Cloudy	10.6	750	1.13	1.38 (0.94)	1.13 (0.94)	0.0	-1.0	0
C <sub>10</sub>	13	Hazy clear	12.4	926	1.31	2.95 (1.77)	1.92 (1.77)	+0.2	-0.5	-3
C <sub>10</sub>	17	Clear	13.6	1102	1.47	5.98 (7.87)	3.66 (3.66)	+0.2	-0.5	-3

† Appearance of 1.0 g/L aqueous surfactant solution.

‡ Hydrophil-lipophil balance (HLB) by Griffin formula; % EO/5 = HLB.

§ Molecular weight.

¶ Molecular area (nm²) per molecule, calculated from the molar volume (V) in mL.  $V = MW/sp. gr.$  where  $sp. gr. = 1.17 g/mL$ .  $nm^2 = (1.09) [(V \times 10^{21})/N]^{2/3}$  where  $10^{21}$  converts V from mL to nm³ and N is Avogadro's number.

# Molecular area from adsorption isotherms; ( ) = Langmuir plots.

†† Capillary rise (cm); (+) hydrophilic; (-) hydrophobic. Estimated accuracy = ±0.2 cm.

‡‡ Sedimentation volume difference (cm³); (sample-blank). Estimated accuracy = ±0.5 cm³.

§§ Turbidity (arbitrary units); (-) = clearer than blank, (+) = more turbid than blank.

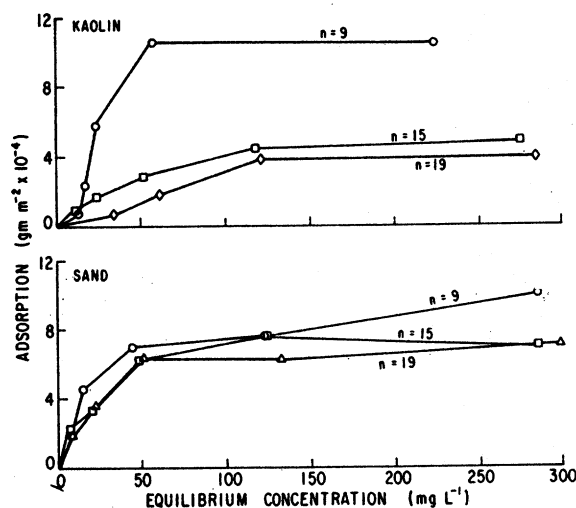


Fig. 2. Adsorption isotherms of (*N*-octyl)(*N*-polyethoxylated)*p*-*t*-butylphenylsulfonamides on sand and kaolin at pH 6.0 in aqueous solution; (*n*) equals number of ethoxy groups.

cles, possibly by hydrophobic interaction. In general, the hexyl derivatives had very little tendency to disperse, as can be seen from the turbidity results. In contrast to the C<sub>6</sub> surfactant with seven ethoxy groups, the compound with *n* = 14 imparted some wettability to the surface of the sand. In this case (*n* = 14) the adsorption of a larger number of EO groups per hydrophobic side chain could result in a slightly more hydrophilic surface than for the *n* = 7 case. Charge neutralization of the surface by the EOH<sup>+</sup> groups and hydrophobic interaction between the (relatively fewer) hydrocarbon side chains could still result in a sediment of particles and relatively little tendency to disperse, however.

Figure 2 shows the results of increasing ethoxy content on a similar series of surfactants but with an octyl in place of the hexyl side chain. Adsorption isotherms show decreased adsorption with increasing ethoxy content (above *n* = 5) but for sand the difference isn't as pronounced as for the compounds described in Fig. 1. The derivative where *n* = 5 (not shown) had limited solubility and no measurable adsorption. The isotherms in Fig. 2 appear similar to the common Langmuir type with an initial steep rise in adsorption sloping off (concave to the concentration axis) to a plateau. This suggests that the C<sub>8</sub> side chain surfactants have higher affinities for the surface of sand and kaolin than do the C<sub>6</sub> surfactants.

Figure 3 gives the results of substituting a decyl in place of the octyl side chain into the surfactant molecule. Surfactant adsorption again decreased significantly with higher ethoxy content above *n* = 5, which had poor solubility and no measurable adsorption. These decyl derivatives also exhibit near Langmuir type adsorption as did the previous set with the octyl side chain. Comparing the initial shape of these isotherm curves with those of Giles' in Parfitt and Rochester (1983) indicate an even stronger surfactant affinity for the adsorbent's surface than the previous set of surfactants. This is seen clearly at the lower surfactant concentrations in the range 0 to 20 mg/L where the isotherms rise almost vertically from the origin. The results shown in Fig. 1, 2, and 3 show an increased adsorption affinity with increasing side chain length in the order hexyl < octyl < decyl. Since the water solubilities of the side chains are in the order hexyl > octyl > decyl, this suggests that at least part of the driving force of adsorption is due to a poor surfactant water interaction in the bulk compared to the surfac-

tant-water interaction in the surface phase as discussed by Kronberg (1983).

The areas/molecule for the adsorbed surfactant were estimated by two methods for the various derivatives and the results are given in Table 1. The molecular areas in parenthesis were determined by linear Langmuir plots and the other areas were estimated from the "plateau" in the adsorption plots. In most cases the plateau did not reach the asymptotic adsorption limit, hence most areas estimated directly from the graphs are somewhat larger than those calculated from the Langmuir plots. The area/molecule given in column 6 of Table 1 provides a useful guide as to the likely orientation of the adsorbed species. By calculating the area from the molar volume we have, in effect, assumed that the adsorbate consists of a hexagonal close packed set of spherical molecules of molar volume  $V$  each molecule of which occupies an area,  $\text{nm}^2$ , on the surface of the adsorbent as discussed by Lowell (1979). Observed areas smaller than this calculated value suggests that the adsorbed molecules have an extended shape and are oriented with the long axis normal to the surface. Where the areas observed are larger than the calculated value an extended molecule lying flat is suggested. Clearly, most of the observed areas in this work suggest an extended molecule with at least part of its structure lying flat on the surface of the adsorbent.

The apparent area per surfactant molecule adsorbed is shown to rise with the number of ethoxy groups in the molecule for all systems. It can be seen, however, that in most cases, as the ethoxy content is increased the area per molecule adsorbed increases more than might be predicted from higher ethoxy content alone. In the case of the  $C_{10}$  system on kaolin, for example, one molecule with 17 ethoxy groups seems to occupy four times as much surface area as one molecule with nine ethoxy groups. If only the EO groups in the surfactant were adsorbing, it might be expected that doubling the ethoxy groups would double the surface area per molecule. This straight forward interpretation is observed only for  $C_8$  on sand where the EO ratios are 9:15:19 and the area ratios are 9:16:18. Clearly this simple model does not suffice to explain the area/molecule data for most of the surfactants studied here. This is not surprising in view of the many interactions possible in such complex systems.

The capillary rise data in Table 1 show that the  $C_8$  derivatives gave generally more wettability when adsorbed on sand than either the  $C_6$  or the  $C_{10}$  derivatives. This means that the surfactant increases the surface hydrophilicity and suggests that the EO groups may be sticking out from the adsorbent surface into the aqueous phase. The sedimentation volume difference and turbidity data clearly show that of the three series of surfactants examined the  $C_8$  surfactants impart the greatest dispersing power to kaolin. The  $n = 9$  surfactant derivative produced a milky dispersion with kaolin that was stable for  $>3$  h. Sedimentation volume difference and turbidity data indicate that all members of the  $C_{10}$  set are poor dispersants. Some surface alkyl chain interaction may aid in kaolin particle coalescence in this system.

Also given in Table 1 are the calculated hydro-

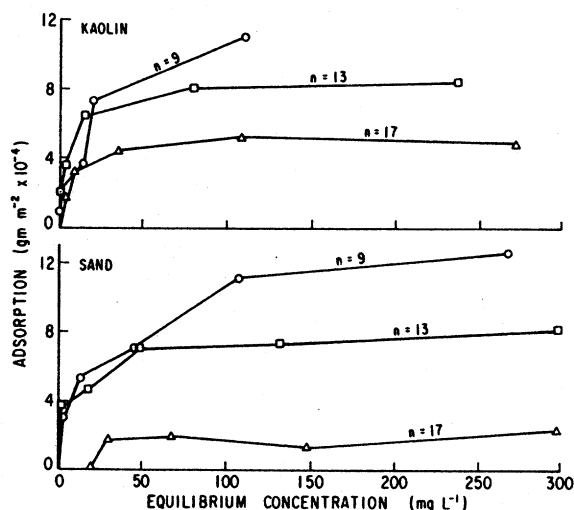


Fig. 3. Adsorption isotherms of (*N*-decyl)(*N*-polyethoxylated)*p*-*t*-butylphenylsulfonamides on sand and kaolin at pH 6.0 in aqueous solution; ( $n$ ) equals number of ethoxy groups.

philic-lipophilic balances (HLB) and the appearance of 1 to 2 mM aqueous surfactant solutions. These results are similar to the literature (Rosen, 1978) and confirm that above HLB 13 one obtains clear solution.

From this work with sand and kaolin it can be stated that for aqueous solutions of alkyl oxyethylated phenyl sulfonamides: (i) As the number of ethoxy groups in the molecule is increased beyond a minimum number for solubility, a corresponding decrease in surfactant surface adsorption is observed. (ii) As the hydrocarbon side chain is lengthened, there is an increasing hydrophobic attraction for the surface. (iii) Type S adsorption offers the best mechanism for hexyl derivatives but octyl and decyl derivatives are better described by Langmuir (L2) adsorption. (iv) The sulfonamide surfactant with the octyl group in the side chain and  $n = 9$  has the best surfactant characteristics of adsorption, wetting, and dispersion of the compounds studied here.

In conclusion, it is clear that optimum use of nonionic surfactants as soil conditioners depends not only on their nonionic character but also on molecular structure. Further research is ongoing with other substituted oxyethylated phenylsulfonamides to determine what effects these structural modifications have on the adsorption onto sand and kaolin as well as soils.

## REFERENCES

- Abe, R., and H. Kuno. 1962. The adsorption of polyoxyethylated nonylphenol on carbon black in aqueous solution. *Kolloid Z. Z. Polym.* Band 181, Heft 1:70.
- Clunie, J.S., and B.T. Ingram. 1983. Adsorption of nonionic surfactants. p. 105-152. *In* G.D. Parfitt and C.H. Rochester (ed.) *Adsorption from solution at the solid/liquid interface*. Academic Press, New York.
- Figdore, P.E. 1982. Adsorption of surfactants on Kaolinite: NaCl versus CaCl<sub>2</sub> salt effects. *J. Colloid Interface Sci.* 87(2):500-517.
- Hsiao, L., and H.N. Dunning. 1955. A comparative study of nonionic detergent adsorption radiotracer, spectrophotometric and surface tension methods. *J. Phys. Chem.* 59(4):362-366.
- Kronberg, B. 1983. Thermodynamics of adsorption of nonionic surfactants on latexes. *J. Colloid Interface Sci.* 96:55-68.
- Kuno, H., and R. Abe. 1961. The adsorption of polyoxyethylated

- nonylphenol on calcium carbonate in aqueous solution. *Kolloid Z. Z. Polym.*, Band 177, Heft 1:40-44.
- Law, J.P., Jr., and G.W. Kunze. 1966. Reactions of surfactants with montmorillonite: Adsorption mechanisms. *Soil Sci. Soc. Am. Proc.* 30:321-327.
- Letey, J. 1975. The use of nonionic surfactants on soils. p. 145-154. *In* W.C. Moldenhauer (ed.) *Experimental Methods and Uses of Soil Conditioners*, Soil Conditioners Symp. Proc. Las Vegas, NV. 15-16 Nov. 1973. Soil Science Society of America, Madison, WI.
- Letey, J., J.F. Osborn and N. Valoras. 1975. Soil water repellency and the use of nonionic surfactants. University of California, Davis.
- Lowell, S. 1979. Adsorbate cross-sectional areas. p. 40-45. *In* S. Lowell (ed.) *Introduction to powder surface area*, Wiley-Interscience, New York.
- Micich, T.J., and W.M. Linfield. 1984. Oxyethylated sulfonamides as nonionic soil wetting agents. *J. Am. Oil Chem. Soc.* 61(3):591-595.
- Parfitt, G.D., and C.H. Rochester. 1983. Adsorption of small molecules. p. 3-47. *In* G.D. Parfitt and C.H. Rochester (ed.) *Adsorption from solution at the solid/liquid interface*. Academic Press, New York.
- Rosen, M.J. 1978. Adsorption of surface-active agents at interfaces: The electrical double layer. p. 26-82. *In* M.J. Rosen (ed.) *Surfactants and interfacial phenomena*. Wiley-Interscience, New York.
- Schott, H. 1968. Interactions in the system: Clay-detergent-cellulose. *J. Am. Oil Chem. Soc.* 45:414-422.
- Valoras, N., J. Letey, and J.F. Osborn. 1969. Adsorption on nonionic surfactants by soil materials. *Soil Sci. Soc. Am. Proc.* 33:345-348.
- Weil, J.K., R.E. Koos, W.M. Linfield, and N. Parris. 1979. Nonionic wetting agents. *J. Am. Oil Chem. Soc.* 56(9):873-877.